2006

(207)Pb Spin-Lattice Relaxation in Solid PbMoO(4) and PbCl(2)

Peter A. Beckmann
Bryn Mawr College, pbeckman@brynmawr.edu

Shi Bai

Alexander J. Vega

Cecil Dybowski

Custom Citation

P.A. Beckmann, S. Bai, A. Vega, and C. Dybowski, *Phys. Rev. B* **74**, 214421 (2006).

^{207}Pb spin-lattice relaxation in solid $PbMoO_4$ and $PbCl_2$

Peter A. Beckmann,[1,2,*] Shi Bai,[1] Alexander J. Vega,[1] and Cecil Dybowski[1]
[1]*Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716, USA*
[2]*Department of Physics, Bryn Mawr College, Bryn Mawr, Pennsylvania 19010, USA*
(Received 29 August 2006; published 21 December 2006)

We have measured the ^{207}Pb nuclear spin-lattice relaxation rate R as a function of temperature T at two nuclear magnetic resonance frequencies ω_0 in the ionic solids lead molybdate ($PbMoO_4$) and lead chloride ($PbCl_2$). R is unexpectedly large, proportional to T^2, and independent of ω_0. Taken together with previous work in lead nitrate [$Pb(NO_3)_2$], these results show that the relaxation does not depend on the nature or rotational motion of the counterion, particularly since the counterion in lead chloride is a single chlorine atom. The theory that explains the observed relaxation rate is reviewed. A second-order Raman process dominates the observed relaxation process. It involves the modulation of the spin-rotation interaction by the lattice vibrations.

DOI: 10.1103/PhysRevB.74.214421 PACS number(s): 76.60.−k, 82.56.Na, 63.20.−e

I. INTRODUCTION

Solid state nuclear magnetic resonance (SSNMR) relaxation experiments provide information on inter- and intramolecular dynamics in many types of solids.[1,2] The association of relaxation with a particular dynamical process depends critically on identifying the mechanism of random modulation of the nuclear magnetic environment. For spin-1/2 nuclei, the modulation of a variety of spin-lattice interactions[1,2] leads to nuclear spin relaxation: the nuclear dipole-dipole interaction, the chemical-shielding-anisotropy interaction, the scalar-coupling interaction or conduction electrons, the spin-rotation interaction, and a direct coupling of nuclear spins to paramagnetic centers. A determination of the dominant relaxation mechanism (the interaction *and* its modulation) relies on experimental hallmarks such as the dependence of the nuclear spin-lattice relaxation rate R on parameters such as temperature T, the NMR frequency $\omega_0 = \gamma B$ (for nuclear magnetogyric ratio γ and applied static magnetic field B), or concentration (of, say, an impurity). It is often assumed that the random process that modulates the interaction is thermally activated, which gives R an exponential dependence on T^{-1}.[1,2] In the fast motion limit, only the chemical-shielding-anisotropy mechanism exhibits a dependence on NMR frequency, being proportional to ω_0^2. A dependence of R on T and/or ω_0 other than these indicates a very different mechanism for relaxation.

The ^{207}Pb relaxation rate constant in $Pb(NO_3)_2$ in the solid state follows:[3]

$$R = AT^2, \tag{1}$$

where A is independent of ω_0. Earlier measurements of R in $Tl(NO_3)_2$ show a similar result.[4] The effectiveness of the observed nuclear spin-lattice relaxation is unusual and unexpected ($T_1 = R^{-1}$ values of order of seconds rather than hours at room temperature) for solids without paramagnetic impurities or large-scale molecular motions. As reviewed below,[5] a time-dependent spin-rotation magnetic field caused by angular oscillations of the internuclear vectors due to lattice vibrations predicts Eq. (1), and this mechanism appears to be responsible for the nuclear spin-lattice relaxation.

In this paper, we report nuclear spin-lattice relaxation rates R for ^{207}Pb in $PbMoO_4$ and $PbCl_2$. Among the many predominantly ionic lead compounds that are available, we chose $PbMoO_4$ because the MoO_4 anion is a tetrahedral group whereas the NO_3 anion in $Pb(NO_3)_2$ is planar. We chose $PbCl_2$ because the anion is a single atom. $PbMoO_4$ and $PbCl_2$, along with $Pb(NO_3)_2$ provide three very different anion environments. In addition, lead spectra tend to be very broad and the experiments can take many days of continuous spectrometer operation. $PbMoO_4$ and $PbCl_2$ have "reasonable" line widths as discussed in the experimental section and this is an important consideration. Finally, both $PbMoO_4$ and $PbCl_2$ are stable and come in only one crystalline form.

The experiments reported here demonstrate that the Raman relaxation mechanism is active in all these ionic lead materials. They also demonstrate that the relaxation efficiency is not strongly affected by the nature of the lead's counterion as A in Eq. (1) varies only slightly among the chloride, nitrate, and molybdate ions. Whereas one might try to construct models whereby the reorientational motions in the NO_3 groups in $Pb(NO_3)_2$ and $Tl(NO_3)_2$ or the MoO_4 group in $PbMoO_4$ might be responsible for the relaxation, this cannot be the case for the Cl atom in $PbCl_2$. We conclude, therefore, that the detailed Raman relaxation model for nuclear spin relaxation[5] is applicable to many heavy spin-1/2 nuclei in a wide range of ionic solids.

II. A BRIEF REVIEW OF THE THEORY

We have presented a detailed theory for the nuclear spin-lattice relaxation rate in systems like lead molybdate and lead chloride.[5] This theory predicts a relaxation rate given by Eq. (1). Here we review the main points of this theory with the intention of highlighting its conceptual basis. The model adopts previous work[3,6] in that it assumes that relaxation is caused by a Raman process involving the interactions between nuclear spins and lattice vibrations via a local, time-dependent, spin-rotation magnetic field $\Delta B(t)$. This field is generated by the relative rotational motion of adjacent atoms participating in transverse vibrational modes. The model places an emphasis on the relation between the local time-

dependent spin-rotation magnetic field $\Delta B(t)$ and the time-dependent angular velocity $\Omega(t)$ of a vibrating atom pair in a solid, in contrast to the conventional description of the spin-rotation interaction of gas molecules where the interaction is related to the angular momentum J. In solid structures, the moment of inertia of a small structural subunit is not well defined and, as such, J is not a meaningful parameter. In a simplified scalar representation, the spin-rotation field is written $\Delta B(t)=\Gamma\Omega(t)$. Thus the spin-rotation interaction is characterized by the magnetorotation constant Γ, rather than by the traditional spin rotation constant C. The magnetorotation constant is determined by the electronic properties of the atoms and the nature of their chemical bonds. Since it is difficult to predict the size of Γ for a small atomic cluster embedded in a solid matrix, we have resorted to order-of-magnitude estimations based on the Γ values of small molecules containing the same nuclei and for which the spin-rotation constants C are known.[5] For freely rotating molecules, the spin-rotation and magnetorotation constants are related through $\hbar\gamma\Gamma=-CI_m$ where I_m is the moment of inertia and γ is the gyromagnetic ratio. Comparison of resulting values across the Periodic Table reveals that the average size of Γ is strongly correlated with the atomic weight, ranging from $\sim 10^{-16}$ T s for hydrogen to $\sim 10^{-13}$ T s for lead.

As a result of the high density of vibrational mode frequencies in a solid, $\Omega(t)$ and $\Delta B(t)$ are randomly fluctuating parameters that can drive nuclear spin-lattice relaxation. Only modes with frequencies in the vicinity of the NMR frequency ω_0 contribute to the relaxation process. Since ω_0 is typically five orders of magnitude smaller than the highest acoustical frequencies, the density of vibrational modes around ω_0 is extremely small, such that the so-called direct process, which is driven by local field fluctuations is highly ineffective. An alternative process is a Raman process where, in addition to the angular velocity Ω, the magnetorotation constant Γ is also modulated by crystal vibrations. This is brought about by the fluctuating strain of the immediate environment of the nucleus under consideration. For instance, when the distance between adjacent atoms changes from the equilibrium length a to a slightly distorted length $a+d$, the magnetorotation constant changes from Γ_0 to $\Gamma=\Gamma_0(1-\varepsilon d)$, the change being described by the coefficient ε. The fluctuation of ΔB due to two simultaneous vibrational modes affecting Γ and Ω, respectively, allows all pairs of modes whose frequencies differ by ω_0 to participate in the relaxation process. As a result, this Raman process is the dominant relaxation pathway for many heavy spin-1/2 nuclei. Using a general theory of nuclear spin relaxation and assuming that the statistics of the crystal vibrations conform to the Debye model, one can calculate the value of A in Eq. (1) to be

$$A=\frac{2\pi\sqrt{2}\gamma^2a^2\varepsilon^2\Gamma_0^2\omega_D k_B^2}{7m^2v^4}. \tag{2}$$

Here, a is the average spacing between the relaxing nucleus and adjacent atoms, m is the average mass of the atoms in the compound, ω_D is the Debye frequency, v is the speed of sound in the material, and k_B is Boltzmann's constant.

The parameter Γ_0 is poorly known and so is ε. Rough estimates of Γ_0 from spin-rotation constants of comparable gas molecules and of ε from comparison with a few calculated values published in the literature, allow A to be predicted only to within one or two orders of magnitude.[5] However, this theory[5] is an important development in the understanding of this Raman relaxation process and the prediction that the observed nuclear spin-lattice relaxation rate R is proportional to T^2 and independent of ω_0 is an important advancement.

III. THE EXPERIMENTS

Polycrystalline samples of $PbMoO_4$ and $PbCl_2$ were purchased from Sigma-Adrich and their quoted purities were 99.999%. Measurements of the ^{207}Pb nuclear spin-lattice relaxation rates R for $PbMoO_4$ and $PbCl_2$ were carried out at 62.6 MHz on a Bruker MSL-300 NMR spectrometer (7.0491 T, with a corresponding proton resonance frequency of 300.130 MHz). The $\pi/2$ pulse width was 2.8 μs. R values were also measured at 41.7 MHz on a Tecmag Discovery NMR spectrometer (4.6954 T, with a corresponding proton resonance frequency of 199.916 MHz and $\pi/2$ pulse width of 3.4 μs). Appropriate phase cycling was used. The NMR spectrum of $PbMoO_4$ is about 150 ppm wide, which is 9.4 kHz at 7.05 T and 6.3 kHz at 4.70 T. The NMR spectrum of $PbCl_2$ is about 550 ppm wide, which is 34 kHz at 7.05 T and 23 kHz at 4.70 T.

In determining spin-lattice relaxation rates R, magnetization-recovery curves at both $\omega_0/2\pi=62.6$ MHz and 41.7 MHz were observed using two techniques, both of which gave the same R values within experimental uncertainty. It is important to apply the same perturbation across the spectrum and to observe the signal in the same way across the spectrum. The first technique was inversion-recovery repeated with phase cycling of the acquisition. It is specifically designed for broad spectra, much broader, in fact than maximum widths of tens of kHz being investigated here. The four parts of the cycle are:

$$\begin{aligned}
&\pi-t-\{\qquad\quad \pi/2-\tau_1-\pi\}-\tau_2-\text{acquire}(+)-\tau_{\text{delay}}-\\
&\pi-t-\{\pi-\tau_3-\pi/2-\tau_1-\pi\}-\tau_2-\text{acquire}(-)-\tau_{\text{delay}}-\\
&\qquad\{\qquad\quad \pi/2-\tau_1-\pi\}-\tau_2-\text{acquire}(-)-\tau_{\text{delay}}-\\
&\qquad\{\pi-\tau_3-\pi/2-\tau_1-\pi\}-\tau_2-\text{acquire}(+)-\tau_{\text{delay}}-.
\end{aligned} \tag{3}$$

This detection sequence consists of a spin-echo experiment, but with alternate inversion by insertion of a π pulse and acquisition-phase switching to cancel the effects of acoustic ringing. The third and fourth lines are a standard acquisition sequence of the type used by Neue *et al.*[7] The added leading π pulse in each of the first two lines inverts the magnetization for creation of the nonequilibrium state required for a standard inversion-recovery sequence. By combining the four sequences with appropriate receiver-phase cycling, the resulting difference signal is directly observed,

$$\Delta M(t) = M(\infty) - M(t) = 2M(\infty)e^{-Rt}. \quad (4)$$

The two short delays, τ_1 and τ_2, are between 15 and 20 μs and τ_3 is about 1 ms.[8]

A second method based on the traditional saturation-recovery procedure was also used. In the sequence, a train of 20 closely space $\pi/2$ pulses is followed by a variable delay, after which the signal is detected with the spin-echo sequence using alternate inversion. The pulse sequence is

$$[\pi/2 - \tau_4 - \pi/2 - \tau_4 \ldots \pi/2] - t - \{\pi/2 - \tau_1 - \pi\} - \tau_2 - \text{aquire}(+) - \tau_5 - ,$$

$$[\pi/2 - \tau_4 - \pi/2 - \tau_4 \ldots \pi/2] - t - \{\pi - \tau_3 - \pi/2 - \tau_1 - \pi\} - \tau_2 - \text{aquire}(-) - \tau_5 - , \quad (5)$$

with τ_4 set to about 5 μs and τ_5 set to about 100 ms. For this saturation-recovery experiment, the saturated (i.e., zeroed) magnetization relaxes towards its equilibrium value according to

$$M(t) = M(\infty)[1 - e^{-Rt}]. \quad (6)$$

The fact that the saturation method and the inversion-recovery method gave the same values for R is reassuring. The relaxation was observed to be exponential, within experimental uncertainty, in all cases. Typically about eight values of t were employed, but a few experiments were performed using about 20 t values over a large range of t to carefully check the exponentiality. Each R measurement took between two and five days of continuous spectrometer operation.

Temperatures above room temperature were achieved by blowing heated, dry nitrogen gas over the sample. Temperatures below room temperature were achieved by blowing heated cold nitrogen gas boiled off from a liquid nitrogen source. Temperature was measured by monitoring the proton spectrum of a very small volume of ethylene glycol $[OH(CH_2)_2OH]$ (above room temperature) or methanol (CH_3OH) (at or below room temperature). For measurements at 62.6 MHz on the Bruker MSL 300, each liquid was contained in a small glass bulb in the center of the sample. For measurements at 41.7 MHz on the Tecmag Discovery, the variable-temperature system was calibrated with these liquids in separate experiments. The chemical-shift difference $\Delta\delta$ between the various proton peaks for both liquids is temperature dependent.[9,10] As a secondary check of the temperature, on several occasions we also observed the chemical shift of the peak in the spectrum of $Pb(NO_3)_2$, which is a known function of temperature.[11]

IV. RESULTS AND DISCUSSION

The solid-state ^{207}Pb spin-lattice relaxation rate R versus T^2 for $PbMoO_4$ and $PbCl_2$ is shown in Fig. 1. For both samples, we calculated R by integrating the spectrum over four different frequency ranges in the spectrum. To within experimental uncertainty (about ±5%), all four R values were the same and gave the same result as integrating over the entire spectrum. Therefore, there is no profile dependence of R. The $PbMoO_4$ data are fitted by linear least-squares analysis to give

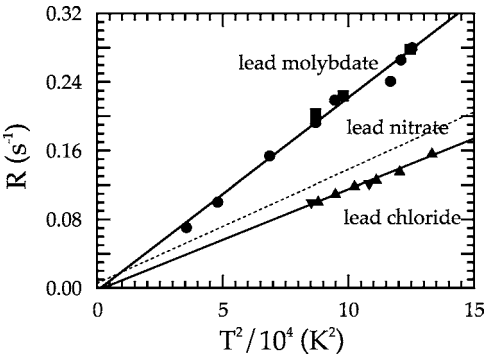

FIG. 1. The solid state ^{207}Pb spin-lattice relaxation rate R vs T^2 for $PbMoO_4$ (● 62.6 MHz, ■ 41.7 MHz) and $PbCl_2$ (▼ 62.6 MHz, ▲ 41.7 MHz). The dashed line summarizing the data for $Pb(NO_3)_2$ is taken from Ref. 3.

$$R = [(2.25 \pm 0.08) \times 10^{-6}\ \text{s}^{-1}\ \text{K}^{-2}]T^2 + [-0.003 \pm 0.008\ \text{s}^{-1}]. \quad (7)$$

Similarly the $PbCl_2$ data are fitted with

$$R = [(1.18 \pm 0.07) \times 10^{-6}\ \text{s}^{-1}\ \text{K}^{-2}]T^2 + [-0.003 \pm 0.007\ \text{s}^{-1}]. \quad (8)$$

Within experimental uncertainty, both intercepts are zero. For comparison, the relaxation rate of $Pb(NO_3)_2$ at several frequencies was fitted by the dashed line in Fig. 1, given by[3]

$$R = [(1.33 \pm 0.03) \times 10^{-6}\ \text{s}^{-1}\ \text{K}^{-2}]T^2 + [-0.0056 \pm 0.0030\ \text{s}^{-1}]. \quad (9)$$

For lead compounds, reasonable numerical estimates of the parameters in Eq. (2) lead to $A = 10^{-7}$–10^{-5} s^{-1} K^{-2}, in agreement with these experimental results.[5] Unfortunately, our understanding of the way local structure affects the values of the various constants in Eq. (2) is insufficient for an interpretation of the different relaxation rates of lead nitrate, lead molybdate, and lead chloride, in terms of the electronic environments of the lead ion in these three compounds. A difference of a factor of two in the values of A implies that the nature of the anion does not strongly affect the lead nuclear spin-lattice relaxation rate.

V. CONCLUSION

The ^{207}Pb spin-lattice relaxation rates R of ^{207}Pb in $PbMoO_4$ and $PbCl_2$ have been investigated as a function of temperature and magnetic field strength. The similarities of these dependences to those observed for $Pb(NO_3)_2$ (Ref. 3) and $Tl(NO_3)_2$ (Ref. 4) shows that the relaxation is not a strong function of the type of anion partner. The observed relaxation is consistent with a Raman-process model of nuclear spin relaxation for spin-1/2 nuclei mediated by the spin-rotation interaction.[5] It is predicted that this mechanism

will only be active for spin-1/2 nuclei with sufficiently large magnetorotation constants, and this presumably correlates closely with the number of electrons. We have previously investigated ^{111}Cd and ^{113}Cd in cadmium molybdate[12] and in cadmium iodide[13] and determined that the Raman spin-rotation process is absent on a scale that observes the relaxation over 1000 s following a perturbation to the Cd nuclear spin system, presumably because the magnetorotation constant Γ is too small. It will be interesting to determine which other heavy-metal spin-1/2 nuclei are strongly affected by this mechanism.

ACKNOWLEDGMENTS

C.R.D. and P.A.B. acknowledge the support of the National Science Foundation under Grants No. CHE-0411790 and No. CHE-0411907.

*Email address: pbeckman@brynmawr.edu

[1] A. Abragam, *Principles of Nuclear Magnetism* (Clarendon, Oxford, 1961).
[2] C. P. Slichter, *Principles of Magnetic Resonance*, 3rd ed. (Springer-Verlag, Berlin, 1992).
[3] J. B. Grutzner, K. Stewart, R. Wasylishen, M. Lumsden, P. A. Beckmann, and C. Dybowski, J. Am. Chem. Soc. **123**, 7094 (2001).
[4] A. Avogadro and M. Villa, Phys. Status Solidi B **75**, 179 (1976).
[5] A. J. Vega, P. A. Beckmann, S. Bai, and C. Dybowski, preceding paper, Phys. Rev. B **74**, 214420 (2006).
[6] R. J. Fitzgerald, M. Gatzke, D. C. Fox, G. D. Cates, and W. Happer, Phys. Rev. B **59**, 8795 (1999).
[7] G. Neue, D. Barich, M. Smith, and C. Dybowski, Solid State Nucl. Magn. Reson. **3**, 115 (1994).
[8] G. Neue, M. L. Smith, M. A. Hepp, D. L. Perry, and C. Dybowski, Solid State Nucl. Magn. Reson. **6**, 241 (1996).
[9] A. L. van Geet, Anal. Chem. **42**, 679 (1970).
[10] A. L. van Geet, Anal. Chem. **40**, 2227 (1968).
[11] P. A. Beckmann and C. Dybowski, J. Magn. Reson. **146**, 379 (2000).
[12] P. A. Beckmann, S. Bai, and C. Dybowski, Phys. Rev. B **71**, 012410 (2005).
[13] P. A. Beckmann, S. Bai, and C. Dybowski (unpublished).